NASA CONTRACTOR REPORT

THEORETICAL RESEARCH PROGRAM TO STUDY CHEMICAL REACTIONS IN AOTV BOW SHOCK TUBES

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16. Abstract

The main focus of this work was the development, implementation, and calibration of methods for performing molecular electronic structure calculations to high accuracy. These various methods were then applied to a number of chemical reactions and species of interest to NASA, notably in the area of combustion chemistry.

Among the development work undertaken was a collaborative effort to develop a program to efficiently predict molecular structures and vibrational frequencies using energy derivatives. Another major development effort involved the design of new atomic basis sets for use in chemical studies: these sets were considerably more accurate than those previously in use. Much effort was also devoted to calibrating methods for computing accurate molecular wave functions, including the first reliable calibrations for realistic molecules using full CI results.

A wide variety of application calculations were undertaken. One area of interest was the spectroscopy and thermochemistry of small molecules, including establishing small molecule binding energies to an accuracy rivaling, or even on occasion surpassing, the experiment. Such binding energies are essential input to modeling chemical reaction processes, such as combustion. Studies of large molecules and processes important in both hydrogen and hydrocarbon combustion chemistry were also carried out. Finally, some effort was devoted to the structure and spectroscopy of small metal clusters, with applications to materials science problems.

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The main focus of the work carried out under Cooperative Agreement NCC2-371 was the development, implementation, and calibration of methods for performing molecular electronic structure calculations to a high degree of accuracy. These various methods were then applied to a number of chemical reactions and species of interest to NASA, notably in the area of combustion chemistry.

Among the development work undertaken was a collaborative effort (with several Scandinavian quantum chemists) to develop a program to efficiently predict molecular structures and vibrational frequencies using energy derivatives. This program exploits molecular symmetry using symmetry-adapted functions and can handle MCSCF wave functions. These combination of capabilities is unique. Another major development effort involved the design of new atomic basis sets for use in chemical studies. These "atomic natural orbital" sets were considerably more accurate than those previously in use, and they were utilized extensively by the entire NASA-Ames Computational Chemistry Branch in performing accurate quantum chemical calculations, as well as by outside researchers. Much effort was also devoted to calibrating methods for computing accurate molecular wave functions, including the first reliable calibrations for realistic molecules using full CI results. The full CI calculations were possible only on the NAS Facility CRAY-2 at the time (1985-1986), and they attracted considerable attention.

A wide variety of application calculations were undertaken. One area of interest was the spectroscopy and thermochemistry of small molecules, including establishing small molecule binding energies to an accuracy rivaling, or even on occasion surpassing, the experiment. Among the species studied was the radical CN, whose binding energy had been a long-standing controversy in the spectroscopy community, and the CH bond energy in acetylene, where two sets of conflicting experimental results were available. Our calculations resolved both these controversies. It may be noted that such binding energies are essential input to modeling chemical reaction processes, such as combustion. Among the more important

spectroscopic investigations were the rotation-vibration intensities (dipole moment function) of OH, a species important as a thermometric probe, and the electronic spectroscopy of diatomic aluminum halides, with relevance to radiation signatures. Studies of large molecules and processes important in both hydrogen and hydrocarbon combustion chemistry were also carried out, including binding energy studies of CH and NH bonds, and mechanistic studies of reactions important in prompt NO_x formation ($CH + N_2$) and in hydrocarbon combustion (acetylene pyrolysis). Finally, some effort was devoted to the structure and spectroscopy of small metal clusters, with applications to materials science problems, and to computing properties that influence nonlinear optical properties: polarizabilities and hyperpolarizabilities.

The following publications have resulted from this work:

(1) C.W. Bauschlicher, S.R. Langhoff, P.R. Taylor, and H. Partridge, *"A Full CI Treatment of Ne atom - a Benchmark Calculation performed on the NAS CRAY-2,"* Chem. Phys. Lett. **126**, 436, 1986.

(2) C.W. Bauschlicher, S.R. Langhoff, P.R. Taylor, N.C. Handy and P.J. Knowles, *"Benchmark Full CI Calculations of HF and NH_2,"* J. Chem. Phys. **85**, 1469, 1986.

(3) C.W. Bauschlicher, S.R. Langhoff, H. Partridge, and P.R. Taylor, *"On the Electron Affinity of the Oxygen Atom,"* J. Chem. Phys. **85**, 3407, 1986.

(4) C.W. Bauschlicher and P.R. Taylor, *"Benchmark Full Calculations of an H_2O, F, and F^-,"* J. Chem. Phys. **85**, 2779, 1986.

(5) P.R. Taylor, *"Integral Processing in Beyond-Hartree-Fock Calculations,"* Int. J. Quantum Chem. **31**, 521, 1987.

(6) P.R. Taylor and C.W> Bauschlicher, *"Strategies for Obtaining the Maximum Performance from Current Supercomputers,"* Theor. Chim. Acta **71**, 105, 1987.

(7) C.W. Bauschlicher and P.R. Taylor, *"A Full CI Treatment of the $^1A_1$ - $^3B_1$ Separation in Methylene,"* J. Chem. Phys. **85**, 6510, 1986.

(8) C.W. Bauschlicher and P.R. Taylor, *A Full CI Treatment of the $^1A_1$, $^1B_1$ and $^3B_1$ States of SiH_2,"* J. Chem. Phys. **86**, 1420, 1987.

(9) C.W. Bauschlicher and P.R. Taylor, *"Full CI Studies of the Collinear Transition State for the Reaction F + H_2 --> HF + H,"* J. Chem. Phys. **86**, 858, 1987.

(10) C.W. Bauschlicher and P.R. Taylor, *"Full CI Benchmark Calculations for Molecular Properties,"* Theor. Chim. Acta, **71**, 263, 1987.

(11) C.W. Bauschlicher and P.R. Taylor, *"Full CI Benchmark Calculations for Several States of the Same Symmetry,"* J. Chem. Phys. **86**, 2844, 1987.

(12) C.W. Bauschlicher and P.R. Taylor, *"Full CI Benchmark Calculations for CH_3,"* J. Chem. Phys. **86**, 5600, 1987.

(13) J. Almlöf and P.R. Taylor, *"General Contraction of Gaussian Basis Sets: I. Atomic Natural Orbits for First- and Second-Row Atoms,"* J. Chem. Phys. **86**, 4070, 1987.

(14) S.R. Langhoff, C.W. Bauschlicher, and P.R. Taylor, *"Accurate ab-initio Calculations on the Ground States of N_2, O2, and F_2,"* Chem. Phys. Lett. **135**, 543, 1987.

(15) S.R. Langhoff, C.W. Bauschlicher, and P.R. Taylor, *"Theoretical Study of the Dipole Moment Function of OH (X^2Pi),"* J. Chem. Phys. **86**, 6992, 1987.

(16) C.W. Bauschlicher, H. Partridge, S.R. Langhoff, P.R. Taylor, and S.P. Walch, *"Accurate ab-initio Calculations which Demonstrate a ^3Pi_u Ground State for Al_2,"* J. Chem. Phys. **86**, 7007, 1987.

(17) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"On the $^1A_1$ - $^3B_1$ Separations in CH_2 and SiH_2,"* J. Chem. Phys. **87**, 387, 1987.

(18) C.W. Bauschlicher, S.R. Langhoff, H. Partridge, T. Halicioglu, and P.R. Taylor, *"Theoretical Approaches to Metal Chemistry,"* in *Supercomputer Research in Chemistry and Chemical Engineering*, (ACS Symposium Series 353), ed. K.F. Jensen and D.G. Truhlar (American Chemical Society, Washington, 1987.

(19) P.R. Taylor and H. Partridge, *"Theoretical Determination of the Ground State of N_2^{2+},"* J. Phys. Chem. **91**, 6148, 1987.

(20) C.W. Bauschlicher and P.R. Taylor, *"Symmetry and Equivalence Restrictions in Electronic Structure Calculations,"* Theor. Chim. Acta. **74**, 63, 1988.

(21) C.W. Bauschlicher and P.R. Taylor, *"Comment on "New Theoretical Description of the Carbon-Carbon Triple Bond,"* Phys. Rev. Lett. **60**, 859, 1988.

(22) J. Almlöf, T. Helgaker, and P.R. Taylor, *"Gaussian Basis Sets for High-Quality ab-initio Calculations,"* J. Phys. Chem. **92**, 3029, 1988.

(23) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"Theoretical Studies of the Electron Affinities of Cu, Cu_2, and Cu_3,"* J. Chem. Phys. **88**, 1041, 1988.

(24) C.W. Bauschlicher, S.P. Walch, S.R. Langhoff, P.R. Taylor and R.L. Jaffe, *"Theoretical Studies of the Potential Surface for the F + H_2 --> HF + H Reaction,"* J. Chem. Phys. **88**, 1743, 1988.

(25) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"Core-Core and Core-Valence Correlation,"* J. Chem. Phys. **88**, 2540, 1988.

(26) D.G. Leopold, J. Almlöf, W.C. Lineberger, and P.R. Taylor *"A Simple Interpretation of the Fe_2^- Photoelectron Spectrum,"* J. Chem. Phys. **88**, 3780, 1988.

(27) S.R. Langhoff, C.W. Bauschlicher, P.R. Taylor, *"Theoretical Studies of AlF, AlCl, and AlBr,"* J. Chem. Phys. **88**, 5715, 1988.

(28) P. Bowen-Jenkins, L.G.M. Petterson, P. Siegbahn, J. Almlöf, and P.R. Taylor, *"On the Bond Distance in Methane,"* J. Chem. Phys. **88**, 6977, 1988.

(29) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"Theoretical Study of the Dissociation Energy and Red and Violet Band Systems of CN,"* Astrophys. J. **332**, 531, 1988.

(30) P.R. Taylor, C.W. Bauschlicher, and S.R. Langhoff, *"The ^2D Rydberg Series in Al I,"* J. Phys. B, **21**, L333, 1988.

(31) C.W. Bauschlicher, L.A. Barnes, and P.R. Taylor, *"The Lowest Ionization Potentials of Al_2,"* J. Phys. Chem. **93**, 2932, 1989.

(32) P.R. Taylor, A. Komornicki, and D.A. Dixon, *"Hexagonal H_6,"* J. Amer. Chem. Soc. **111**, 1259, 1989.

(33) C.W. Bauschlicher, S.R. Langhoff, P.R. Taylor, *"Recent Developments in the Calculation of ab-initio Potential Energy Surfaces,"* in: *Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules* (NATO ASI Series), ed. A. Lagana (Kluwer, Dordrecht, 1989).

(34) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"On the Electron Affinities of the Ca, Sc, Ti, and Y Atoms,"* Chem. Phys. Lett. **158**, 245, 1989.

(35) C.W. Bauschlicher, S.R. Langhoff, T.J. Lee, and P.R. Taylor, *"The Effect of Higher than Double Excitations on the F + H_2 --> HF + H Barrier,"* J. Chem. Phys. **90**, 4296, 1989.

(36) P.R. Taylor, C.W. Bauschlicher, and D.W. Schwenke, *"Chemical Calculations on Cray Computers,"* in: *Methods in Computational Chemistry, Vol. 3, Concurrent Computation in Chemical Calculations*, ed. S. Wilson (Plenum, New York, 1089) -- invited review article.

(37) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"Accurate Quantum Chemical Calculations,"* Adv. Chem. Phys., **77**, 103, 1990 -- invited review article.

(38) J. Almlöf, B.J. DeLeeuw, P.R. Taylor, C.W. Bauschlicher, and P. Siegbahn, *"The Dissociation Energy of N_2,"* Int. J. Quantum Chem. Symp. **23**, 345, 1989.

(39) T.J. Lee and P.R. Taylor, *"Theoretical Investigations of the Properties of Coupled Cluster Wave Functions,"* Int. J. Quantum Chem. Symp. **23**, 199, 1989.

(40) S.R. Langhoff, C.W. Bauschlicher, and P.R. Taylor, *"Theoretical Study of the Dipole Moment Function of OH ($X\ ^2Pi$),"* J. Chem. Phys. **91**, 5953, 1989.

(41) J. Almlöf and P.R. Taylor, *"General Contraction of Gaussian Basis Sets: II. Atomic Natural Orbitals and the Calculation of Atomic and Molecular Properties,"* J. Chem. Phys. **92**, 551, 1990.

(42) P.R. Taylor, T.J. Lee, J.E. Rice, and J. Almlöf, *"The Polarizabilities of Ne,"* Chem. Phys. Lett. **163**, 359, 1989.

(43) T.J. Lee, A.P. Rendell, and P.R. Taylor, *"Theoretical Investigations of the Structures and Binding Energies of Be_n and Mg_n (n=3-5) Clusters,"* J. Chem. Phys. **92**, 489, 1990.

(44) T.J. Lee, A.P. Rendell, and P.R. Taylor, *"Comparison of the Quadratic Configuration Interaction and Coupled Cluster Methods Including Triple Excitations,"* J. Phys. Chem. **94**, 3928, 1990.

(45) C.W. Bauschlicher, P.R. Taylor, and A. Komornicki, *"The Vibrational Frequencies pf TiF_nCl_{4-n} (n=0-4),"* J. Chem. Phys. **92**, 3928, 1990.

(46) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"On the Dissociation Energy of BH,"* J. Chem. Phys. **93**, 502, 1990.

(47) A.P. Rendell, T.J. Lee, and P.R. Taylor, *"Vibrational Frequencies for Be_3 and Be_4,"* J. Chem. Phys. **93**, 7050, 1990.

(48) C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *The C-H Bond Dissociation Energyu of Acetylene,"* Chem. Phys. Lett., **171**, 42, 1990.

(49) K.G. Dyall, K. Faegri, and P.R. Taylor, *"Polyatomic Molecular Dirac-Hartree-Fock Calculations with Gaussian Basis Sets,"* in: *The effects of Relativity in Atoms, Molecules, and the Solid State*, ed. S. Wilson (Plenum, New York, 1991).

(50) T.J. Lee, A.P. Rendell, and P.R. Taylor, *"Vibrational Frequencies of Mg Clusters,"* J. Chem. Phys. **93**, 6636, 1990.

(51) J.D. Watts, I. Cernusak, J. Noga, R.J. Bartlett, C.W. Bauschlicher, T.J. Lee, A.P. Rendell, and P.R. Taylor, *"Triple Excitation Contributions to the Binding in Ve Clusters: Calibration Calculations on Be_3,"* J. Chem. Phys. **93**, 8875, 1990.

(52) D.W. Schwenke, S.P. Walch, and P.R. Taylor, *"A Potential energy Surface for H_2 and H_2O: Ab-initio calculations and Analytical Representation,"* J. Chem. Phys. **94**,2986, 1991.

(53) J. Almlöf and P.R. Taylor, *"Atomic Natural Orbital Basis Sets for LCAO Calculations,"* Adv. Quantum Chem., (in press) -- invited article.

(54) J.E. Rice, P.R. Taylor, T.J. Lee, and J. Almlöf, *"An Accurate Determination of the Dipole Polarizabilities and Hyperpolarizabilities of the Noble Gases,"* J. Chem. Phys. **94,** 4972, 1991.

(55) P.R. Taylor, J.M.L. Martin, J.-P. Francois, and R. Gijbels, *"An ab-initio study of the C_3^+ Cation Using Multireference Methods,"* J. Phys. Chem. **95**, 6530, 1991.

(56) K.G. Dyall, P.R. Taylor, K. Faegri, and H. Partridge, *"All-Electron Molecular Dirac-Hartree-Fock Calculations: I. Formalism, Implementation, and Application to the Group IV Tetrahydrides,"* J. Chem. Phys. **95**, 2583, 1991.

(57) S.R. Langhoff, C.W. Bauschlicher, and P.R. Taylor, *"Bond Dissociation Energies of Sincly, Doubly, and Tripli Bonded Systems,"* Chem. Phys. Lett. **180**, 88, 1991.

(58) T. Helgaker and P.R. Taylor, *"On the Evaluation of Derivatives of Gaussian Integrals,"* Theor. Chim. Acta, in press.

(59) T.J. Lee, A.P. Rendell, and P.R. Taylor, *"The Structures, Binding Energies and Vibrational Frequencies of Ca_3 and Ca_4 -- and Application of the CCSD(T) Method,"* Theor. Chim. Acta, in press.

(60) H. Partridge, C.W. Bauschlicher, S.R. Langhoff, and P.R. Taylor, *"Theoretical Study of the Low-Lying Bound States of O2,"* J. Chem. Phys. **95**, 8292, 1991.

(61) J.F. Stanton, J. Gauss, R.J. Bartlett, T. Helgaker, P. Jorgensen, H.J. Jensen, and P.R. Taylor, *"Interconversion of Diborane(4) Isomers,"* J. Phys. Chem. in press.

(62) A. Komornicki, D.A. Dixon, and P.R. Taylor, *"Concerted Hydrogen Atom Exchange Between Three HF Molecules,"* J. Chem. Phys., in press

(63) J.E. Rice, G.E. Scuseria, T.J. Lee, P.R. Taylor, and Almlöf, *"Connected Triple Excitations in Coupled-Cluster Calculations of Hyperpolarizabilities: Neon,"* Chem. Phys. Lett., in press.

(64) C.W. Bauschlicher and P.R. Taylor, *"Atomic Natural Orbital Basis Sets for Transition Metals,"* Theor. Chim. Acta, in press.

(65) J.M.L. Martin, T.J.Lee, G.E. Scuseria, and P.R. Taylor, *"Ab-initio Multireference Study of the BN Molecule,"* J. Chem. Phys., in press.

(66) J.M.L. Martin, T.J. Lee, and P.R. Taylor, *"An Accurate ab-initio- Quartic Force Field for Ammonia,"* J. Chem. Phys., submitted for publication.